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(54) Title: PERFUMABLE DRY CLEANING AND SPOT REMOVAL COMPOSITION (57) Abstract Efficient dry cleaning compositions with pleasant odor qualities comprise water, butoxy propoxy propanol cleaning solvent and a perfume ingredient. The compositions also comprise 1,2-octanediol as a wetting agent, and a polyacrylate emulsifier. Dry cleaning sheets impregnated with the composition are suitable for in-home use.		

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FIELD OF THE INVENTION

CROSS-REFERENCE TO RELATED APPLICATION

BACKGROUND OF THE INVENTION

20 While solvent-based dry cleaning processes are quite effective for removing oily soils and stains, they are not optimal for removing particulates such as clay soils, and may require special treatment conditions to remove proteinaceous stains. Ideally, particulates and proteinaceous stains are removed from fabrics using detergent ingredients and operating conditions which are more akin to aqueous laundering processes than to conventional dry cleaning.

30 As can be seen from the foregoing, and aside from the effects on certain fabrics such as woolens, there are no special, inherent advantages for solvent-based immersion dry cleaning over aqueous cleaning processes with respect to fabric cleaning or refreshment. Moreover, on a per-garment basis, commercial dry cleaning is much more expensive than aqueous cleaning processes.

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a variety of cleaning ingredients, including some solvents.

There are certain limitations to the formulation of both dry cleaning and spot remover compositions, especially when such compositions are intended for use in the home. In particular, safe and effective cleaning ingredients which are not malodorous are required for such compositions. 5 Unfortunately, many excellent dry cleaning solvents have noxious odors and would not be tolerated for home use.

By the present invention, it has been discovered that butoxy propoxy propanol (BPP) not only is an acceptable solvent with regard to its odor qualities, but also is an excellent cleaner for soiled fabrics. Importantly, BPP's odor characteristics allow it to be combined with perfume 10 ingredients to provide cleaning compositions which have pleasant odor qualities.

BACKGROUND ART

Dry cleaning processes are disclosed in: EP 429,172A1, published 29.05.91, Leigh, et al.; and in U.S. 5,238,587, issued 8/24/93, Smith, et al. Other references relating to dry cleaning compositions and processes, as well as wrinkle treatments for fabrics, include: GB 1,598,911; and 15 U.S. Patents 4,126,563, 3,949,137, 3,593,544, 3,647,354; 3,432,253 and 1,747,324; and German applications 2,021,561 and 2,460,239, 0,208,989 and 4,007,362. Cleaning/pre-spotting compositions and methods are also disclosed, for example, in U.S. Patents 5,102,573; 5,041,230; 4,909,962; 4,115,061; 4,886,615; 4,139,475; 4,849,257; 5,112,358; 4,659,496; 4,806,254; 5,213,624; 4,130,392; and 4,395,261. Sheet substrates for use in a laundry dryer are disclosed in 20 Canadian 1,005,204. U.S. 3,956,556 and 4,007,300 relate to perforated sheets for fabric conditioning in a clothes dryer. U.S. 4,692,277 discloses the use of 1,2-octanediol in liquid cleaners.

SUMMARY OF THE INVENTION

The present invention encompasses a cleaning composition especially adapted for use on fabrics; comprising:

- 25 (a) at least about 4%, by weight, of butoxy propoxy propanol;
- (b) an aesthetic amount of a perfume ingredient;
- (c) at least about 60%, by weight, of water;
- (d) an emulsifier;
- (e) optionally, a deterative surfactant; and
- 30 (f) optionally, 1,2-octanediol.

A preferred composition herein comprises from about 5% to about 25%, by weight, of butoxy propoxy propanol, from about 75% to about 95%, by weight, of water, and from about 0.5% to about 1.5%, by weight, of perfume.

The invention also encompasses an article of manufacture, comprising an integral substrate 35 releasably containing or having releasably affixed thereto a cleaning composition comprising butoxy propoxy propanol. The substrate used herein is preferably lint-resistant and is most preferably polyester based. Such articles are conveniently in the form of a pad or sheet.

A preferred article for dry cleaning is wherein said cleaning composition comprises:

- (a) at least about 7%, by weight, of butoxy propoxy propanol;
- (b) at least about 0.5%, by weight, of a perfume;
- (c) at least about 80%, by weight, of water; and
- 5 (d) no more than about 0.2%, by weight, of a polyacrylate emulsifier.

A highly preferred dry cleaning article according to this invention is in the form of a lint-resistant pad or sheet, wherein said cleaning composition comprises from about 5% to about 25%, by weight, of butoxy propoxy propanol and from about 75% to about 95%, by weight, of water.

All percentages, ratios and proportions herein are by weight, unless otherwise specified.

- 10 All documents cited are, in relevant part, incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The ingredients of the dry cleaning compositions and their use in the process of the present invention are described seriatim hereinafter.

- Cleaning Compositions - The chemical compositions which are used to provide the
- 15 cleaning function in the present dry cleaning and spot removal processes comprise ingredients which are safe and effective for their intended use. Since the processes herein do not involve an aqueous rinse step, the cleaning compositions employ ingredients which do not leave undesirable residues on fabrics when employed in the manner disclosed herein. Moreover, since the dry cleaning process may be carried out in a hot air clothes dryer, the compositions contain only ingredients whose flash
- 20 points render them safe for such use. The cleaning compositions do contain water, since water not only aids in the cleaning function, but also can help remove wrinkles and restore fabric drape and appearance, especially in hot air dryers. While conventional laundry detergents are typically formulated to provide good cleaning on cotton and cotton/polyester blend fabrics, the cleaning compositions herein must be formulated to also safely and effectively clean and refresh fabrics such
- 25 as wool, silk, rayon, rayon acetate, and the like.

- In addition, the cleaning compositions herein comprise ingredients which are specially selected and formulated to minimize dye removal from the fabrics being cleaned. In this regard, it is recognized that the solvents typically used in immersion dry cleaning processes can remove some portion of certain types of dyes from certain types of fabrics. However, such removal is tolerable in
- 30 immersion processes since the dye is removed relatively uniformly across the surface of the fabric. In contrast, it has now been determined that high concentrations of certain types of cleaning ingredients at specific sites on fabric surfaces can result in unacceptable localized dye removal. The preferred cleaning compositions herein are formulated to minimize or avoid this problem.

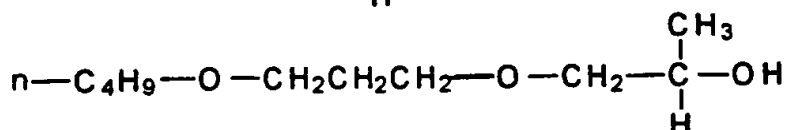
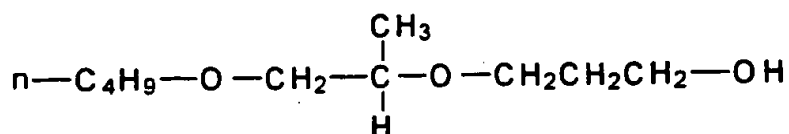
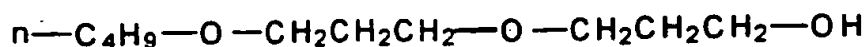
- The dye removal attributes of the present cleaning compositions can be compared with art-
- 35 disclosed cleaners using photographic or photometric measurements, or by means of a simple, but effective, visual grading test. Numerical score units can be assigned to assist in visual grading and to allow for statistical treatment of the data, if desired. Thus, in one such test, a colored garment

(typically, silk which tends to be more susceptible to dye loss than most woolen or rayon fabrics) is treated by padding-on cleaner using an absorbent, white paper hand towel. Hand pressure is applied, and the amount of dye which is transferred onto the white towel is assessed visually. Numerical units ranging from: (1) "I think I see a little dye on the towel"; (2) "I know I see some dye
5 on the towel"; (3) I see a lot of dye on the towel"; through (4) "I know I see quite a lot of dye on the towel" are assigned by panelists.

Having due regard to the foregoing considerations, the following illustrates the ingredients used in the cleaning compositions herein, but is not intended to be limiting thereof.

- 10 (a) Solvent - The compositions will comprise at least about 4%, typically from about 5% to about 25%, by weight, of the "BPP" solvent described herein. The objective is to provide at least about 0.4 g, preferably from about 0.5 g to about 2.5 g, of BPP solvent per kg of fabrics being cleaned.
- 15 (b) Perfume - The perfume used herein can be simple and can comprise individual odoriferous ingredients, such as those noted hereinafter, or can comprise complex blends of multiple ingredients which provide a more complex sensory impression. Whether simple or complex, the perfume is used herein in an aesthetic amount. By "aesthetic amount" herein is meant an amount which is sufficient to at least cover the inherent odor of the cleaning composition. Of course, if a highly perfumed composition is desired, more perfume can be added. Typically, the
20 perfume will comprise at least about 0.0001% by weight of the cleaning compositions herein.
- (c) Emulsifier - The cleaning compositions will comprise sufficient emulsifier to provide a stable, homogeneous composition comprising components (a), (b), (d) and (e). For the preferred emulsifiers disclosed hereinafter, levels as low as
25 0.05%, preferably 0.07% to about 0.20%, by weight, are quite satisfactory. If less efficient emulsifiers are used, levels up to about 2%, by weight, can be used, but may leave some noticeable residues on the fabrics.
- (d) Water -The compositions will comprise at least about 60%, typically from about 80% to about 95%, by weight, of water. Stated otherwise, the objective is to
30 provide at least about 6 g of water per kg of fabrics being cleaned.
- (e) Optionals - The compositions herein may comprise various optional ingredients, including conventional surfactants, and the like. If used, such optional ingredients will typically comprise from about 0.1% to about 10%, by weight, of the compositions, having due regard for residues on the cleaned fabrics.

35 The solvent herein is butoxy propoxy propanol (BPP) which is available in commercial quantities as a mixture of isomers in about equal amounts. The isomers, and mixtures thereof, are all useful herein. The isomer structures are as follows:



BPP is outstanding for cleaning; moreover, it allows for the formulation of effective cleaning compositions herein without the use of conventional surfactants. Importantly, the odor of BPP is of a degree and character that it can be relatively easily masked by conventional perfume ingredients. While BPP is not completely miscible with water and, hence, could negatively impact processing of the cleaning compositions herein, that potential problem has been successfully overcome by means of the PEMULEN-type polyacrylate emulsifiers, as disclosed hereinafter.

It has now been determined that 1,2-octanediol ("OD") also affords special advantages in the formulation of the cleaning compositions herein. From the standpoint of aesthetics, OD is a relatively innocuous and low odor material. Moreover, OD appears to volatilize from fabric surfaces without leaving visible residues. This is especially important in a dry cleaning process of the present type which is conducted without a rinse step. From the performance standpoint, OD appears to function both as a solvent for greasy/oily stains and as what might be termed a "pseudo-surfactant" for particulate soils and water-soluble stains. Whatever the physical-chemical reason, OD has now been found to be a superior wetting agent with respect to both cleaning and ease-of-use in the present context of home-use cleaning compositions and processes.

The BPP solvent used herein is preferably a mixture of the aforesaid isomers. The BPP solvent is so effective for cleaning that it allows the amount of relatively expensive ingredients such as 1,2-octanediol to be minimized. In a preferred mode, the cleaning compositions comprise a mixture of the 1,2-octanediol and BPP, at a weight ratio of OD:BPP in the range of from about 1:250 to about 2:1, preferably from about 1:200 to about 1:5.

In view of the superior odor characteristics of the BPP solvent employed herein, the formulator has the luxury of choosing from a wide variety of perfume ingredients in order to arrive at a perfumed formulation. The perfumed formulations herein can be prepared from perfume ingredients including, but not limited to: 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene; ionone methyl; ionone gamma methyl; methyl cedrylone; methyl dihydrojasmonate; methyl 1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; para-hydroxy-phenyl-butanone; benzophenone; methyl beta-naphthyl ketone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; 7-

hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecane; condensation products of hydroxycitronellal and methyl anthranilate, condensation products of hydroxycitronellal and indol, condensation products of phenyl acetaldehyde and indol; 2-methyl-3-(para-tert-butylphenyl)-propionaldehyde; ethyl vanillin; heliotropin; hexyl cinnamic aldehyde; amyl cinnamic aldehyde; 2-methyl-2-(para-iso-propylphenyl)-propionaldehyde; coumarin; decalactone gamma; cyclopentadecanolide; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8-hexamethylcyclopenta-gamma-2-benzopyrane; beta-naphthol methyl ether; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; tricyclodecenyl propionate; tricyclodecenyl acetate; benzyl salicylate; cedryl acetate; and para-(tert-butyl) cyclohexyl acetate; anisaldehyde; and vanillin.

Other perfume materials include essential oils, resinoids, and resins from a variety of sources including but not limited to orange oil, lemon oil, patchouli, Peru balsam, Olibanum resinoid, styrax, labdanum resin, nutmeg, cassia oil, benzoin resin, coriander, lavandin and lavender. Still other perfume chemicals include phenyl ethyl alcohol, terpineol and mixed pine oil terpenes, linalool, linalyl acetate, geraniol, nerol, 2-(1,1-dimethylethyl)-cyclohexanol acetate, benzyl acetate, orange terpenes, eugenol, and diethylphthalate.

While the perfume ingredients disclosed herein and others may be combined in various ways, according to the desires and aesthetic needs of the formulator, the following are given by way of illustration, and not limitation, of complex perfumes which can be used herein. The perfumes A, B and C of Table I are shown with their Perfume Ingredients and amounts of each ingredient (as % weight). Blends of A, B and C may also be used.

TABLE I

<u>Perfume Ingredient</u>		<u>A</u>	<u>B</u>	<u>C</u>
25	Hexyl cinnamic aldehyde 10.0	--	5.0	
	2-methyl-3-(para-tert-butylphenyl)-propionaldehyde	5.0	5.0	--
	7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetra-			
	methyl naphthalene 5.0	10.0	10.0	
	Benzyl salicylate 5.0	--	--	
30	7-acetyl-1,1,3,4,4,6-hexamethyltetralin	10.0	5.0	10.0
	Para-(tert-butyl) cyclohexyl acetate	5.0	5.0	--
	Methyl dihydro jasmonate --	5.0	--	
	Beta-naphthol methyl ether	--	0.5	--
	Methyl beta-naphthyl ketone	--	0.5	--
35	2-methyl-2-(para-iso-propylphenyl)-propionaldehyde	--	2.0	--
	1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-			
	cyclopenta-gamma-2-benzopyrane	--	9.5	--

	Dodecahydro-3a,6,6,9a-tetramethylnaphtho[2,1b]furan	—	—	0.1
	Anisaldehyde	—	—	0.5
	Coumarin	—	—	5.0
	Cedrol	—	—	0.5
5	Vanillin —	—	5.0	
	Cyclopentadecanolide	3.0	—	10.0
	Tricyclodecenyl acetate —	—	2.0	
	Labdanum resin —	—	2.0	
	Tricyclodecenyl propionate	—	—	2.0
10	Phenyl ethyl alcohol	20.0	10.0	27.9
	Terpineol	10.0	5.0	—
	Linalool	10.0	10.0	5.0
	Linalyl acetate	5.0	—	5.0
	Geraniol	5.0	—	—
15	Nerol	—	5.0	—
	2(1,1-dimethylethyl)-cyclohexanol acetate	5.0	—	—
	Orange oil, cold pressed —	5.0	—	
	Benzyl acetate	2.0	2.0	—
	Orange terpenes —	10.0	—	
20	Eugenol —	1.0	—	
	Diethylphthalate —	9.5	—	
	Lemon oil, cold pressed =	=	<u>10.0</u>	
	Total	100.0	100.0	100.0

A highly preferred emulsifier herein is commercially available under the trademark

25 PEMULEN, The B. F. Goodrich Company, and is described in U.S. Patents 4,758,641 and 5,004,557, incorporated herein by reference. PEMULEN polymeric emulsifiers are high molecular weight polyacrylic acid polymers. The structure of PEMULEN includes a small portion that is oil-loving (lipophilic) and a large water-loving (hydrophilic) portion. The structure allows PEMULEN to function as a primary oil-in-water emulsifier. The lipophilic portion adsorbs at the oil-water

30 interface, and the hydrophilic portion swells in the water forming a network around the oil droplets to provide emulsion stability. An important advantage for the use of such polyacrylate emulsifiers herein is that cleaning compositions can be prepared which contain solvents or levels of solvents that are otherwise not soluble or readily miscible with water. A further advantage is that effective emulsification can be accomplished using PEMULEN-type emulsifier at extremely low usage levels

35 (0.05-0.2%), thereby minimizing the level of any residue left on fabrics following product usage. For comparison, typically about 3-7% of conventional anionic or nonionic surfactants are required to stabilize oil-in-water emulsions, which increases the likelihood that a residue will be left on the

fabrics. Another advantage is that emulsification (processing) can be accomplished effectively at room temperature.

While the cleaning compositions herein function quite well with only the BPP, perfume, Pemulen, water, and optional OD, they may also optionally contain deterative surfactants to further enhance their cleaning performance. While a wide variety of deterative surfactants such as the C₁₂-C₁₆ alkyl sulfates and alkylbenzene sulfonates, the C₁₂-C₁₆ ethoxylated (EO 0.5-10 avg.) alcohols, the C₁₂-C₁₄ N-methyl glucamides, and the like can be used herein, it is highly preferred to use surfactants which provide high grease/oil removal. Included among such preferred surfactants are the C₁₂-C₁₆ alkyl ethoxy sulfates (AES), especially in their magnesium salt form, and the C₁₂-C₁₆ dimethyl amine oxides. An especially preferred mixture comprises MgAE₁S/MgAE_{6.5}S/C₁₂ dimethyl amine oxide, at a weight ratio of about 1:1:1. If used, such surfactants will typically comprise from about 0.05% to about 2.5%, by weight, of the cleaning compositions herein.

In addition to the preferred solvents and other ingredients disclosed above, the cleaning compositions herein may comprise various optional ingredients, such as preservatives, co-solvents, brighteners, salts for viscosity control, pH adjusters or buffers, anti-static agents, softeners, colorants, mothproofing agents, insect repellents, and the like.

Carrier - When used in a home dry cleaning mode the foregoing cleaning compositions are preferably used in combination with a carrier, such that the cleaning composition performs its function as the surfaces of the fabrics being cleaned come in contact with the surface of the carrier.

The carrier can be in any desired form, such as powders, flakes, shreds, and the like. However, it will be appreciated that such comminuted carriers would have to be separated from the fabrics at the end of the cleaning process. Accordingly, it is highly preferred that the carrier be in the form of an integral pad or sheet which substantially maintains its structural integrity throughout the cleaning process. Such pads or sheets can be prepared, for example, using well-known methods for manufacturing non-woven sheets, paper towels, fibrous batts, cores for bandages, diapers and catamenials, and the like, using materials such as wood pulp, cotton, rayon, polyester fibers, and mixtures thereof. Woven cloth pads may also be used, but are not preferred over non-woven pads due to cost considerations. Integral carrier pads or sheets may also be prepared from natural or synthetic sponges, foams, and the like.

The carriers are designed to be safe and effective under the intended operating conditions of the present process. The carriers must not be flammable during the process, nor should they deleteriously interact with the cleaning composition or with the fabrics being cleaned. In general, non-woven polyester-based pads or sheets are quite suitable for use as the carrier herein.

The carrier used herein is most preferably lint-resistant. By "lint-resistant" herein is meant a carrier which resists the shedding of visible fibers or microfibers onto the fabrics being cleaned, i.e., the deposition of what is known in common parlance as "lint". A carrier can easily and adequately be judged for its acceptability with respect to lint-resistance by rubbing it on a piece of

dark blue woolen cloth and visually inspecting the cloth for lint residues.

The lint-resistance of sheet or pad carriers used herein can be achieved by several means, including but not limited to: preparing the carrier from a single strand of fiber, and employing known bonding techniques commonly used with nonwoven materials, e.g., point bonding, print bonding, adhesive/resin saturation bonding, adhesive/resin spray bonding, stitch bonding and bonding with binder fibers. In an alternate mode, a carrier can be prepared using an absorbent core, said core being made from a material which, itself, is not lint-resistant. The core is then enveloped within a sheet of porous, lint-resistant material having a pore size which allows passage of the cleaning compositions, but through which lint from the core cannot pass. An example of such a carrier comprises a cellulose or polyester fiber core enveloped in a non-woven polyester scrim.

The carrier should be of a size which provides sufficient surface area that effective contact between the surface of the carrier and the surface of the fabrics being cleaned is achieved. Of course, the size of the carrier should not be so large as to be unhandy for the user. Typically, the dimensions of the carrier will be sufficient to provide a macroscopic surface area (both sides of the carrier) of at least about 360 cm², preferably in the range from about 360 cm² to about 3000 cm². For example, a rectangular carrier may have the dimensions (x-direction) of from about 20 cm to about 25 cm, and (y-direction) of from about 18 cm to about 45 cm.

The carrier is intended to contain a sufficient amount of the cleaning composition to be effective for its intended purpose. The capacity of the carrier for the cleaning composition will vary according to the intended usage. For example, carrier/cleaning composition pads or sheets which are intended for a single use will require less capacity than such pads or sheets which are intended for multiple uses. For a given type of carrier the capacity for the cleaning composition will vary mainly with the thickness or "caliper" (z-direction; dry basis) of the sheet or pad. For purposes of illustration, typical single-use polyester sheets used herein will have a thickness in the range from about 0.1 mm to about 0.7 mm and a basis weight in the range from about 30 g/m² to about 100 g/m². Typical multi-use polyester pads herein will have a thickness in the range from about 0.2 mm to about 1.0 mm and a basis weight in the range from about 40 g/m² to about 150 g/m². Open-cell sponge sheets will range in thickness from about 0.1 mm to about 1.0 mm, and sponge pads will range in thickness from about 1.5 mm to about 2.5 mm. Of course, the foregoing dimensions may vary, as long as the desired quantity of the cleaning composition is effectively provided by means of the carrier.

Container - The present dry cleaning process is conducted using a flexible container. The fabrics to be cleaned are placed within the container with the carrier/cleaning composition article, and the container is agitated, thereby providing contact between the carrier/cleaning composition and the surfaces of the fabrics.

The flexible container used herein can be provided in any number of configurations, and is conveniently in the form of a flexible pouch, or "bag", which has sufficient volume to contain the

fabrics being cleaned. Suitable containers can be manufactured from any economical material, such as polyester, polypropylene, and the like, with the proviso that it must not melt if used in contact with hot dryer air. It is preferred that the walls of the container be substantially impermeable to water vapor and solvent vapor under the intended usage conditions. It is also preferred that such containers be provided with a sealing means which is sufficiently stable to remain closed during the cleaning process. Simple tie strings or wires, various snap closures such as ZIP LOK® closures, and VELCRO®-type closures, contact adhesive, adhesive tape, zipper-type closures, and the like, suffice.

The container can be of any convenient size, and should be sufficiently large to allow tumbling of the container and fabrics therein, but should not be so large as to interfere with the operation of the tumbling apparatus. With special regard to containers intended for use in hot air clothes dryers, the container must not be so large as to block the air vents. If desired, the container may be small enough to handle only a single shirt, blouse or sweater, or be sufficiently large to handle a man's suit.

Process - The present cleaning process can be conducted in any manner which provides mechanical agitation, such as a tumbling action, to the container with the fabrics being cleaned. If desired, the agitation may be provided manually. However, in a convenient mode a container with the carrier/cleaning composition and enveloping the soiled fabric is sealed and placed in the drum of an automatic clothes dryer. The drum is allowed to revolve, which imparts a tumbling action to the container and agitation of its contents concurrently with the tumbling. By virtue of this agitation, the fabrics come in contact with the carrier releasably containing the cleaning composition. It is preferred that heat be employed during the process. Of course, heat can easily be provided in a clothes dryer. The tumbling and optional (but preferred) heating is carried out for a period of at least about 10 minutes, typically from about 20 minutes to about 30 minutes. The process can be conducted for longer or shorter periods, depending on such factors as the degree and type of soiling of the fabrics, the nature of the soils, the nature of the fabrics, the fabric load, the amount of heat applied, and the like, according to the needs of the user.

The following illustrates a typical process in more detail, but is not intended to be limiting thereof.

Example 1

A dry cleaning article in sheet form is assembled using a sheet substrate and a cleaning composition prepared by admixing the following ingredients.

	<u>Ingredient</u>	<u>% (wt.)</u>
	BPP*	7.0
	1,2-octanediol	0.5
35	PEMULEN TR-1**	0.15
	KOH	0.08
	Perfume***	0.75

Water

91.52

*Isomer mixture, available from Dow Chemical Co.

**PEMULEN TR-2, B. F. Goodrich, may be substituted.

***Perfume A, B, C or mixtures thereof may be used.

5 A non-linting carrier sheet is prepared using a non-woven two-ply fabric stock comprising polyester fibers, caliper 0.25 mm to 0.34 mm, basis weight 84 g/m². The fabric is cut into square carrier sheets approximately 25 cm on a side, i.e., 625 cm² sheets. Three or four rows of regularly-spaced 1.27 cm (0.5 in.) diameter circular holes are punched through the sheet. (The finished sheet can later be folded for packaging, and when unfolded and used in the manner disclosed herein, the

10 holes help maintain the sheet in the desired unfolded configuration.)

23 Grams of the above-noted cleaning composition are evenly applied to the sheet by spreading onto the sheet with a roller or spatula using hand pressure. In an alternate mode, the cleaning composition can be applied by dipping or spraying the composition onto the substrate, followed by squeezing with a roller or pair of nip rollers, i.e., by "dip-squeezing" or "spray

15 squeezing".

A dry cleaning sheet of the foregoing type is unfolded and placed flat in a plastic bag having a volume of about 25,000 cm³ together with up to about 2 kg of dry garments to be cleaned. When the garments and the dry cleaning sheet are placed in the bag, the air is preferably not squeezed out of the bag before closing and sealing. This allows the bag to billow, thereby providing

20 sufficient space for the fabrics and cleaning sheet to tumble freely together. The bag is closed, sealed and placed in a conventional hot-air clothes dryer. The dryer is started and the bag is tumbled for a period of 20-30 minutes at a dryer air temperature in the range from about 50°C to about 85°C. During this time, the dry cleaning sheet remains substantially in the desired open position, thereby providing effective contact with the fabrics. After the machine cycle is complete,

25 the bag and its contents are removed from the dryer, and the spent dry cleaning sheet is discarded. The plastic bag is retained for re-use. The garments are cleaned and refreshed. The water present in the cleaning composition serves to minimize wrinkles in the fabrics.

In an alternate mode, heavily soiled areas of the fabric being cleaned can optionally be pre-treated by pressing or rubbing a fresh dry cleaning sheet according to this invention on the area.

30 The sheet and pre-treated fabric are then placed in the container, and the dry cleaning process is conducted in the manner described herein.

The compositions prepared in the manner of this invention can also be directly applied to isolated spots and stains on fabrics in the manner of a spot remover product. The following illustrates this aspect of the invention, but is not intended to be limiting thereof.

35

EXAMPLE II

a spot remover composition comprises the following:

Ingredients% (wt.)

	BPP	7.0
	PEMULEN	0.15
	1,2-Octanediol	0.5
	Surfactant Mixture*	0.25
5	Perfume**	0.75
	Water	Balance

*Mixture of MgAE_1S , $\text{MgAE}_{6.5}\text{S}$ and C_{12} amine oxide, in the range of 1:1:1 to 0.5:1:1.

**A, B or C, as disclosed above.

The composition is directly padded or sprayed onto spots and stains, followed by rubbing, to effect their removal. In an alternate mode, the composition can be gelled or thickened using conventional ingredients to provide a "stick-form" spot remover.

Having thus described and exemplified the present invention, the following further illustrates various cleaning compositions which can be formulated and used in the practice thereof.

EXAMPLE III

15	<u>Ingredient</u>	<u>% (wt.) Formula Range</u>
	BPP*	5-25%
	1,2-Octanediol	0.1-7%
	MgAE_1S	0.01-0.8%
	$\text{MgAE}_{6.5}\text{S}$	0.01-0.8%
20	C_{12} Dimethyl Amine Oxide	0.01-0.8%
	PEMULEN**	0.05-0.20%
	Perfume Ingredient	0.01-1.5%
	Water	Balance

pH Range from about 6 to about 8.

25 *Other organic solvents or co-solvents which can be used herein include various glycol ethers, including materials marketed under trademarks such as Carbitol, methyl Carbitol, butyl Carbitol, propyl Carbitol, and hexyl Cellosolve, methoxy propoxy propanol (MPP), ethoxy propoxy propanol (EPP), propoxy propoxy propanol (PPP), and all isomers and mixtures, respectively, of MPP, EPP, and PPP, and the like, and mixtures thereof. Having due regard for odor shortcomings and safety for in-home use, various conventional chlorinated and hydrocarbon dry cleaning solvents such as 1,2-dichloroethane, trichloroethylene, isoparaffins, and mixtures thereof, are preferably not used herein.

30 **As disclosed in U.S. Patents 4,758,641 and 5,004,557, such polyacrylates include homopolymers which may be crosslinked to varying degrees, as well as non-crosslinked. Preferred herein are homopolymers having a molecular weight in the range of from about 100,000 to about 10,000,000, preferably 200,000 to 5,000,000.

Excellent cleaning performance is secured using any of the foregoing non-immersion processes and articles to provide from about 5 g to about 50 g of the cleaning compositions per

kilogram of fabric being cleaned.

EXAMPLE IV

A dry cleaning composition with reduced tendency to cause dye "bleeding" or removal from fabrics as disclosed above is as follows.

5	<u>INGREDIENT</u>	<u>PERCENT (wt.)</u>	<u>(RANGE)</u>
	Butoxypropoxy propanol (BPP)	7.000	4.0 - 25.0%
	NEODOL 23 - 6.5*	0.750	0.05 - 2.5%
	1,2-Octanediol	0.500	0.1 - 10.0%
	Perfume	0.750	0.1 - 2.0%
10	Pemulen TR-1	0.125	0.05 - 0.2%
	Potassium Hydroxide (KOH)	0.060	0.024 - 0.10
	Potassium Chloride	0.075	0.02 - 0.20
	Water (distilled or deionized)	90.740	60.0 - 95.0%

Target pH = 7.0

- 15 *Shell; C₁₂-C₁₃ alcohol, ethoxylated with average EO of 6.5.

15-25 Grams of a composition of the foregoing type are placed on a carrier sheet for use in the manner disclosed herein. A preferred carrier substrate comprises a binderless (or optional low binder), hydroentangled absorbent material, especially a material which is formulated from a blend of cellulosic, rayon, polyester and optional bicomponent fibers. Such materials are available from
 20 Dexter, Non-Wovens Division, The Dexter Corporation as HYDRASPUN[®], especially Grade 10244. The manufacture of such materials forms no part of this invention and is already disclosed in the literature. See, for example, U.S. Patents 5,009,747, Viazmensky, et al., April 23, 1991 and 5,292,581, Viazmensky, et al., March 8, 1994, incorporated herein by reference. Preferred materials for use herein have the following physical properties.

25		Grade		Optional
		<u>10244</u>	<u>Targets</u>	<u>Range</u>
	Basis Weight	gm/m ²	55	35-75
	Thickness	microns	355	100-1500
	Density gm/cc	0.155	0.1-0.25	
30	Dry Tensile	gm/25 mm		
	MD		1700	400-2500
	CD		650	100-500
	Wet Tensile	gm/25 mm		
	MD*		700	200-1250
35	CD*		300	100-500
	Brightness	%	80	60-90
	Absorption Capacity	%	735	400-900 (H ₂ O)

Dry Mullen gm/cm² 1050 700-1200

*MD - machine direction; CD - cross direction

As disclosed in U.S. 5,009,747 and 5,292,281, the hydroentangling process provides a nonwoven material which comprises cellulosic fibers, and preferably at least about 5% by weight of synthetic fibers, and requires less than 2% wet strength agent to achieve improved wet strength and wet toughness.

Surprisingly, this hydroentangled carrier is not merely a passive absorbent for the cleaning compositions herein, but actually optimizes cleaning performance. While not intending to be limited by theory, it may be speculated that this carrier is more effective in delivering the cleaning composition to soiled fabrics. Or, this particular carrier might be better for removing soils by contact with the soiled fabrics, due to its mixture of fibers. Whatever the reason, improved dry cleaning performance is secured.

In addition to the improved cleaning performance, it has now been discovered that this hydroentangled carrier material provides an additional, unexpected benefit due to its resiliency. In-use, the dry cleaning sheets herein are designed to function in a substantially open configuration. However, the sheets are packaged and sold to the consumer in a folded configuration. It has been discovered that carrier sheets made from conventional materials tend to undesirably revert to their folded configuration in-use. This undesirable attribute can be overcome by perforating such sheet, but this requires an additional processing step. It has now been discovered that the hydroentangled materials used to form the carrier sheet herein do not tend to re-fold during use, and thus do not require such perforations (although, of course, perforations may be used, if desired). Accordingly, this newly-discovered and unexpected attribute of the carrier materials herein makes them optimal for use in the manner of the present invention.

A sheet of the foregoing type is placed together with the fabrics to be dry cleaned in a flexible containment bag having dimensions as noted hereinabove and sealing means. In a preferred mode, the containment bag is constructed of thermal resistant film in order to provide resistance to hot spots (350°F-400°F; 177°C to 204°C) which can develop in some dryers. This avoids internal self-sealing and external surface deformation of the bag, thereby allowing the bag to be re-used.

In a preferred embodiment, 0.0025 mm to 0.0075 mm thickness nylon film is converted into a 26 inch (66 cm) x 30 in. (76 cm) bag. Bag manufacture can be accomplished in a conventional manner using standard impulse heating equipment, air blowing techniques, and the like. In an alternate mode, a sheet of nylon is simply folded in half and sealed along two of its edges.

In addition to thermally stable "nylon-only" bags, the containment bags herein can also be prepared using sheets of co-extruded nylon and/or polyester or nylon and/or polyester outer and/or inner layers surrounding a less thermally suitable inner core such as polypropylene. In an alternate

mode, a bag is constructed using a nonwoven outer "shell" comprising a heat-resistant material such as nylon or polyethylene terephthalate and an inner sheet of a polymer which provides a vapor barrier. The non-woven outer shell protects the bag from melting and provides an improved tactile impression to the user. Whatever the construction, the objective is to protect the bag's integrity under conditions of thermal stress at temperatures up to at least about 400-500°F (204°C to 260°C). Nylon VELCRO®-type, ZIP-LOK®-type and/or zipper-type closures can be used to seal the bag, in-use.

Besides the optional nonionic surfactants used in the cleaning compositions herein, which are preferably C₈-C₁₈ ethoxylated (E01-15) alcohols or the corresponding ethoxylated alkyl phenols, the compositions can contain enzymes to further enhance cleaning performance. Lipases, amylases and protease enzymes, or mixtures thereof, can be used. If used, such enzymes will typically comprise from about 0.001% to about 5%, preferably from about 0.01% to about 1%, by weight, of the composition. Commercial detergent enzymes such as LIPOLASE, ESPERASE, ALCALASE, SAVINASE and TERMAMYL (all ex. NOVO) and MAXATASE and RAPIDASE (ex. International Bio-Synthesis, Inc.) can be used.

If an antistatic benefit is desired, the compositions herein can contain an anti-static agent. If used, such anti-static agents will typically comprise at least about 0.5%, typically from about 2% to about 8%, by weight, of the compositions. Preferred anti-stats include the series of sulfonated polymers available as VERSAFLEX 157, 207, 1001, 2004 and 7000, from National Starch and Chemical Company.

The compositions herein can optionally be stabilized for storage using conventional preservatives such as KATHON® at a level of 0.001%-1%, by weight.

If the compositions herein are used in a spot-cleaning mode, they are preferably pressed (not rubbed) onto the fabric at the spotted area using an applicator pad comprising looped fibers, such as is available as APLIX 200 or 960 Uncut Loop, from Aplix, Inc., Charlotte, NC. An underlying absorbent sheet or pad of looped fibers can optionally be placed beneath the fabric in this mode of operation.

WHAT IS CLAIMED IS:

1. A cleaning composition especially adapted for use on fabrics; characterized in that it comprises:
 - 5 (a) at least 4%, by weight, of butoxy propoxy propanol;
 - (b) an aesthetic amount of a perfume ingredient;
 - (c) at least 60%, by weight, of water;
 - (d) an emulsifier;
 - (e) optionally, a deterative surfactant; and
 - 10 (f) optionally, 1,2-octanediol.
2. A composition according to Claim 1 comprising from 5% to 25%, by weight, of butoxy propoxy propanol and from 75% to 95%, by weight, of water.
- 15 3. A composition according to Claim 1 wherein the emulsifier is a polyacrylate, and wherein said emulsifier comprises no more than 0.2%, by weight, of the composition.
4. An article of manufacture, characterized in that it comprises an integral substrate having releasably containing or having releasably affixed thereto a composition according to Claim
- 20 1.
5. An article according to Claim 4 wherein said substrate is lint-resistant.
6. An article according to Claim 4 in the form of a pad or sheet.
- 25 7. An article according to Claim 4 wherein said cleaning composition comprises:
 - (a) at least 7%, by weight, of butoxy propoxy propanol;
 - (b) at least 0.5%, by weight, of a perfume;
 - (c) at least 80%, by weight, of water; and
 - 30 (d) no more than 0.2%, by weight, of a polyacrylate emulsifier.
8. An article according to Claim 7 wherein said cleaning composition comprises from 5% to 25%, by weight, of butoxy propoxy propanol, and from 75% to 95%, by weight, of water.

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(54) Title: PERFUMABLE DRY CLEANING AND SPOT REMOVAL COMPOSITION (57) Abstract Efficient dry cleaning compositions with pleasant odor qualities comprise water, butoxy propoxy propanol cleaning solvent and a perfume ingredient. The compositions also comprise 1,2-octanediol as a wetting agent, and a polyacrylate emulsifier. Dry cleaning sheets impregnated with the composition are suitable for in-home use.		

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According to International Patent Classification (IPC) or to both national classification and IPC

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 D06L C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 344 847 (THE PROCTER & GAMBLE CO.) 6 December 1989 see page 3, line 28 - page 5, line 27 see claims 1-6,13 ---	1,2
X	EP,A,0 328 174 (THE PROCTER & GAMBLE CO.) 16 August 1989 see page 3, line 9 - line 35 see page 4, line 2 - line 3 see claims 1,2 ---	1,2
A	EP,A,0 539 025 (UNILEVER PLC.) 28 April 1993 see page 6, line 1 - page 7, line 52 see claims 1-3,6 --- -/--	1,3-7

☒ Further documents are listed in the continuation of box C.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 196 146 (FARELLA JOANNA M. ET AL.) 23 March 1993 see column 8, line 55 - line 62 see claims 1,17 ---	1
A	US,A,4 692 277 (SIKLOSI MICHAEL P.) 8 September 1987 cited in the application see table 1 see claims 1-8 ---	1
A	EP,A,0 429 172 (UNILEVER PLC.) 29 May 1991 cited in the application see the whole document ---	4-6
A	US,A,5 238 587 (SMITH JAMES A. ET AL.) 24 August 1993 cited in the application see the whole document -----	4-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/US 96/02883

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0344847	06-12-89	US-A- 4943392 AU-B- 635893 AU-A- 3592089 CA-A- 1321334 JP-A- 2132199	24-07-90 08-04-93 07-12-89 17-08-93 21-05-90
EP-A-0328174	16-08-89	AU-B- 629529 AU-A- 2890689 CA-A- 1330927 DE-D- 68914487 DE-T- 68914487 IE-B- 62760 JP-A- 2147700 US-A- 4966724	08-10-92 03-08-89 26-07-94 19-05-94 06-10-94 22-02-95 06-06-90 30-10-90
EP-A-0539025	28-04-93	US-A- 5246603 AU-B- 664859 AU-A- 2535792 CA-A- 2078717 JP-A- 5222672	21-09-93 07-12-95 01-04-93 26-03-93 31-08-93
US-A-5196146	23-03-93	NONE	
US-A-4692277	08-09-87	AU-B- 603558 AU-A- 6681186 CA-A- 1332909 DK-B- 169133 EP-A- 0227195 GB-A,B 2184453 HK-A- 50693 JP-A- 62240392	22-11-90 25-06-87 08-11-94 22-08-94 01-07-87 24-06-87 04-06-93 21-10-87
EP-A-0429172	29-05-91	AU-B- 629055 AU-A- 6459490 CA-A- 2027148 JP-A- 3130473	24-09-92 18-04-91 17-04-91 04-06-91
US-A-5238587	24-08-93	CA-A- 2135746 EP-A- 0640156 JP-T- 7509629	25-11-93 01-03-95 26-10-95

Information on patent family members

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